

A Three-dimensional Tm(III)-Zn(II) Heteronuclear Metal-organic Framework Based on Imidazole-dicarboxylate Ligand: Synthesis, Crystal Structure and Luminescence Property

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ABSTRACT A *d-f* heteronuclear metal-organic framework (MOF), $\{[\text{Tm}_3\text{Zn}_6(\text{bipy}_2)_2(\text{mimda})_7(\text{H}_2\text{O})_3](\text{H}_2\text{O})_5\}_n$ (**1**, H_3mimda = 2-methyl-1-H-imidazole-4,5-dicarboxylic acid, and bipy = 4,4'-bipyridine), has been synthesized under solvothermal conditions, and structurally characterized by elemental analysis, IR spectra and X-ray single-crystal diffraction. It crystallizes in orthorhombic system, space group *Pnma* with $a = 16.1102(9)$, $b = 33.5805(19)$, $c = 16.8593(10)$ Å, $\beta = 97.344(11)^\circ$, $V = 9120.7(9)$ Å³, $Z = 4$, $F(000) = 5184$, the final $R = 0.0530$ and $wR = 0.1306$. In complex **1**, the Tm(III) ions adopt two types of coordination fashions. Complex **1** shows one-dimensional (1-D) Tm-Zn heteronuclear zigzag chains, and these chains are further linked by H_3mimda ligands into Tm-Zn heteronuclear 2-D lattice-like arrays. The 2-D heteronuclear units were connected through $[\text{Zn}_6(\text{mimda})_6]$ rings to give rise to the Tm-Zn heteronuclear cages. Finally, H_3mimda ligands connected the cages into a 3-D heterometallic framework by the combination of $[\text{TmO}_7]_n$ and Tm-Zn heteronuclear cages. In addition, the thermal stability and luminescent property have been investigated.

Keywords: *d-f* heteronuclear metal-organic frameworks; Tm(III) complex; 2-methyl-1-H-imidazole-4,5-dicarboxylic acid; luminescence;

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1 INTRODUCTION

In recent years, lanthanide-based metal-organic frameworks (MOFs) have increasingly attracted considerable attention because of their intriguing structural topologies and potential applications in gas storage, luminescence and magnetism^[1-6]. Lanthanide metal ions possess high coordination numbers and the long wavelengths range from the visible to the near-infrared region. However, the absorption coefficients are

usually very low with slow emissive rates due to the Laporte forbidden *f-f* transitions^[7, 8]. In order to reduce the effect of this problem, our strategy is to employ the imidazole dicarboxylate ligand as chromophores and transition metal that can improve the energy transition^[9-11]. The imidazole dicarboxylate ligands containing N and O donors are especially popular because they can adopt a variety of coordination modes, which has proven to be an excellent building block for forming a series of MOFs with fascinating structures and useful properties. A large number of imidazole dicarboxylate-based MOFs of transition metal ions have been reported^[12, 13]. On the other hand, introducing pillared rigid ligand containing N atoms such as 4,4'-bipyridine into these MOFs is another effective strategy for producing diversified structure and enhancing the performance of the final MOFs^[14]. However, it is still a challenge to design and construct *d-f* heteronuclear MOFs^[15-18] with dicarboxylate ligands due to the different reaction conditions such pH values, metal/ligand ratio, solvents, and reaction temperature. In this contribution, a new complex, $\{[\text{Tm}_3\text{Zn}_6(\text{bipy})_2(\text{mimda})_7(\text{H}_2\text{O})_3](\text{H}_2\text{O})_5\}_n$ (**1**) based on H_3mimda ligand and bipy has been obtained. In addition, the IR, photoluminescence and thermal stability of **1** have been investigated.

2 EXPERIMENTAL

2.1 Materials and physical measurements

All chemicals and solvents purchased were of reagent grade and used without further purification. Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Model 240 Perkin-Elmer elemental analyzer. The infrared spectrum was performed on an IRAffinity-1S in the range of 3500~500 cm^{-1} . The X-ray powder diffraction pattern (XRPD) of **1** was recorded at 293 K on a Bruker D8 Advance diffractometer ($\text{CuK}\alpha$, $\lambda = 1.54056 \text{ \AA}$) operated at 40 kV and 30 mA, using a Cu-target tube and a graphite monochromator. Thermal gravimetric analysis (TGA) experiments were carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 1200 $^{\circ}\text{C}$ under a nitrogen atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}^{-1}$. The emission/excitation spectra were recorded on an F-7000 (HITACHI) spectrophotometer at room temperature.

2.2 Synthesis of complex **1**

A mixture of Tm_2O_3 (0.05 mmol, 0.0192 g), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0370 g, 0.1 mmol), H_3mimda (0.15 mmol, 0.0270 g) and bipy (0.1 mmol, 0.0170 g) was mixed in a DMF-water solution (10 mL). After that the mixture was added into a Teflon-lined autoclave and heated to 162 $^{\circ}\text{C}$ for 5400 minutes, and then cooled to room temperature. Colorless crystals of **1** were obtained in 0.0048 g yield (48%, based on lanthanide element). Elemental Anal. Calcd. (%) for $\text{C}_{62}\text{H}_{51}\text{N}_{18}\text{O}_{45}\text{Tm}_3\text{Zn}_6$: C, 27.91; H, 1.92; N, 9.45. Found: C, 27.95; H, 1.90; N, 9.47. IR (cm^{-1}): 3340w, 2974m, 2897w, 2367m, 1716w, 1539m, 1388m, 1049m, 887m, 771m.

2.3 Crystal structure determination

A colorless block crystal of complex **1** (0.26mm \times 0.21mm \times 0.18mm) was mounted on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by using a ϕ/ω scan mode at room temperature. A total of 99936 reflections were collected for **1**, of which 10650 ($R_{\text{int}} = 0.0837$) independent reflections in the range of $1.75 \leq \theta \leq 27.50^{\circ}$ with index ranges of

$-20 \leq h \leq 20$, $-43 \leq k \leq 43$ and $-21 \leq l \leq 21$ were collected at 293(2) K. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was solved by direct methods with SHELXS-97^[19]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97^[20]. For complex **1**, disordered methyl carbon atoms of H₃mimda ligands were restrained in order to obtain reasonable thermal parameters^[21]. The final $R = 0.0530$ and $wR = 0.1306$ ($w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 146.3998P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.093$, $(\Delta\rho)_{\text{max}} = 2.776$ and $(\Delta\rho)_{\text{mix}} = -1.150$ e/Å³. The selected bond lengths and bond angles and the hydrogen bond parameters are listed in Tables **1** and **2**, respectively.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Complex 1

Bond	Dist.	Bond	Dist.	Bond	Dist.
Tm(1)–O(1)	2.212(7)	Tm(1)–O(1)#1	2.212(7)	Tm(1)–O(5)	2.255(6)
Tm(1)–O(5)#1	2.255(6)	Tm(1)–O(3)	2.256(7)	Tm(1)–O(3)#1	2.256(7)
Tm(1)–O(1W)	2.361(10)	Tm(2)–O(11)	2.193(6)	Tm(2)–O(9)	2.226(6)
Tm(2)–O(7)	2.283(6)	Tm(2)–O(3W)	2.290(7)	Tm(2)–O(2W)	2.310(8)
Tm(2)–O(13)	2.373(5)	Tm(2)–O(13)#2	2.473(5)	Tm(2)–O(14)#2	2.486(5)
Tm(2)–C(20)#2	2.865(7)	Zn(1)–O(4W)	1.972(10)	Zn(1)–N(2)	2.000(7)
Zn(1)–N(5)#3	2.011(7)	Zn(1)–O(4)	2.100(7)	Zn(1)–O(10)#3	2.138(7)
Zn(2)–N(1)#4	2.046(8)	Zn(2)–N(3)	2.074(7)	Zn(2)–N(6)	2.080(7)
Zn(2)–O(12)	2.171(6)	Zn(2)–O(6)	2.183(6)	Zn(2)–O(2W)	2.229(7)
Zn(3)–N(7)	1.981(7)	Zn(3)–N(4)#5	2.002(7)	Zn(3)–N(8)	2.036(8)
Zn(3)–O(8)#5	2.126(6)	Zn(3)–O(14)	2.318(6)	O(2)–Zn(2)#6	2.229(7)
O(8)–Zn(3)#7	2.126(6)	O(10)–Zn(1)#8	2.138(7)	O(13)–Tm(2)#2	2.473(5)
O(14)–Tm(2)#2	2.486(5)				
Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Tm(1)–O(1)#1	82.1(4)	O(1)–Tm(1)–O(5)	76.6(3)	O(1)–Tm(1)–O(5)	125.6(3)
O(1)–Tm(1)–O(5)#1	125.6(3)	O(1)–Tm(1)–O(5)#1	76.6(3)	O(5)–Tm(1)–O(5)#1	76.5(4)
O(1)–Tm(1)–O(3)	94.9(3)	O(1)–Tm(1)–O(3)	154.6(3)	O(5)–Tm(1)–O(3)	77.4(3)
O(5)–Tm(1)–O(3)	123.6(3)	O(1)–Tm(1)–O(3)#1	154.6(3)	O(1)–Tm(1)–O(3)#1	94.9(3)
O(5)–Tm(1)–O(3)#1	123.6(3)	O(5)–Tm(1)–O(3)#1	77.4(3)	O(3)–Tm(1)–O(3)#1	77.1(4)
O(1)–Tm(1)–O(1W)	78.8(3)	O(1)–Tm(1)–O(1W)	78.8(3)	O(5)–Tm(1)–O(1W)	141.7(2)
O(5)–Tm(1)–O(1W)	141.7(2)	O(3)–Tm(1)–O(1W)	75.9(3)	O(3)–Tm(1)–O(1W)	75.9(3)
O(11)–Tm(2)–O(9)	84.6(2)	O(11)–Tm(2)–O(7)	81.8(3)	O(9)–Tm(2)–O(7)	79.2(2)
O(11)–Tm(2)–O(3W)	114.2(3)	O(9)–Tm(2)–O(3W)	130.9(3)	O(7)–Tm(2)–O(3W)	145.0(2)
O(11)–Tm(2)–O(2W)	79.4(3)	O(9)–Tm(2)–O(2W)	72.6(3)	O(7)–Tm(2)–O(2W)	147.2(2)
O(3W)–Tm(2)–O(2W)	67.7(3)	O(11)–Tm(2)–O(13)	76.9(2)	O(9)–Tm(2)–O(13)	152.4(2)
O(7)–Tm(2)–O(13)	78.0(2)	O(3W)–Tm(2)–O(13)	76.0(3)	O(2W)–Tm(2)–O(13)	122.6(3)
O(11)–Tm(2)–O(13)#2	138.2(2)	O(9)–Tm(2)–O(13)#2	124.2(2)	O(7)–Tm(2)–O(13)#2	75.9(2)
O(3W)–Tm(2)–O(13)#2	71.8(2)	O(2W)–Tm(2)–O(13)#2	134.3(3)	O(13)–Tm(2)–O(13)#2	64.2(2)
O(11)–Tm(2)–O(14)#2	159.4(2)	O(9)–Tm(2)–O(14)#2	77.0(2)	O(7)–Tm(2)–O(14)#2	85.6(2)
O(3W)–Tm(2)–O(14)#2	85.3(3)	O(2W)–Tm(2)–O(14)#2	103.6(3)	O(13)–Tm(2)–O(14)#2	116.29(18)
O(13)–Tm(2)–O(14)#2	52.12(17)	O(11)–Tm(2)–C(20)#2	160.0(3)	O(9)–Tm(2)–C(20)#2	101.4(2)
O(7)–Tm(2)–C(20)#2	80.7(2)	O(3W)–Tm(2)–C(20)#2	76.3(3)	O(2W)–Tm(2)–C(20)#2	120.6(3)
O(13)–Tm(2)–C(20)#2	90.1(2)	O(13)–Tm(2)–C(20)#2	25.95(19)	O(14)–Tm(2)–C(20)#2	26.21(19)
O(4W)–Zn(1)–N(2)	122.8(4)	O(4W)–Zn(1)–N(5)#3	111.9(4)	N(2)–Zn(1)–N(5)#3	125.3(3)
O(4W)–Zn(1)–O(4)	91.9(4)	N(2)–Zn(1)–O(4)	80.3(3)	N(5)–Zn(1)–O(4)	101.3(3)
O(4W)–Zn(1)–O(10)#3	92.6(4)	N(2)–Zn(1)–O(10)#3	95.0(3)	N(5)–Zn(1)–O(10)#3	79.5(3)
O(4)–Zn(1)–O(10)#3	174.8(3)	N(1)–Zn(2)–N(3)	97.4(3)	N(1)–Zn(2)–N(6)	155.9(3)
N(3)–Zn(2)–N(6)	105.9(3)	N(1)–Zn(2)–O(12)	93.6(3)	N(3)–Zn(2)–O(12)	99.5(3)

N(6)–Zn(2)–O(12)	76.9(2)	N(1)–Zn(2)–O(6)	90.1(3)	N(3)–Zn(2)–O(6)	77.8(2)
N(6)–Zn(2)–O(6)	100.5(3)	O(12)–Zn(2)–O(6)	175.7(3)	N(1)–Zn(2)–O(2)–#4	76.0(3)
N(3)–Zn(2)–O(2)–#4	161.0(3)	N(6)–Zn(2)–O(2)–#4	83.5(3)	O(12)–Zn(2)–O(2)–#4	98.6(3)
O(6)–Zn(2)–O(2)–#4	84.4(3)	N(7)–Zn(3)–N(4)–#5	128.9(3)	N(7)–Zn(3)–N(8)	124.6(3)
N(4)–Zn(3)–N(8)	106.5(3)	N(7)–Zn(3)–O(8)–#5	99.1(3)	N(4)–Zn(3)–O(8)–#5	79.9(3)
N(8)–Zn(3)–O(8)–#5	92.2(3)	N(7)–Zn(3)–O(14)	76.8(2)	N(4)–Zn(3)–O(14)	103.6(2)
N(8)–Zn(3)–O(14)	89.2(3)	O(8)–Zn(3)–O(14)	175.7(2)		

Symmetry transformations used to generate the equivalent atoms: #1: $x, -y+1/2, z$; #2: $-x+2, -y, -z+1$; #3: $x-1/2, y, -z+3/2$;

#4: $x+1/2, y, -z+1/2$; #5: $-x+3/2, -y, z-1/2$; #6: $x-1/2, y, -z+1/2$; #7: $-x+3/2, -y, z+1/2$; #8: $x+1/2, y, -z+3/2$

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°) for Complex 1

D–H···A	d(D–H)	d(H···A)	d(D···A)	\angle (DHA)
O(1w)–H(12)···O(7w)	0.84	2.30	2.855(2)	124
O(2w)–H(21)···O(5w) ^{#1}	0.84	2.39	2.917(2)	122
O(3w)–H(32)···O(7) ^{#2}	0.84	2.12	2.757(9)	132
O(4w)–H(41)···O(6w)	0.84	2.33	2.72(2)	109
O(4w)–H(42)···O(6w)	0.84	2.36	2.72(2)	106
C(10)–H(10A)···O(10) ^{#3}	0.96	2.45	3.143(1)	129
C(10)–H(10C)···O(12)	0.96	2.50	3.356(1)	149
C(16)–H(16C)···O(4) ^{#4}	0.96	2.53	3.363(1)	145
C(22)–H(22A)···O(8) ^{#5}	0.96	2.41	3.138(1)	133
C(22)–H(22B)···O(6)	0.96	2.44	3.334(1)	155

Symmetry codes: #1: $1+x, y, z$; #2: $2-x, -y, 1-z$; #3: $-1/2+x, y, 3/2-z$; #4: $1/2+x, y, 3/2-z$; #5: $3/2-x, -y, -1/2+z$

3 RESULTS AND DISCUSSION

3.1 Crystal structure of complex 1

Single-crystal X-ray analysis reveals that **1** crystallizes in orthorhombic system, space group *Pnma*. As shown in Fig. 1, the asymmetric unit of **1** comprises three Zn(II) ions, two Tm(III) ions, four H₃mimda ligands, one bipy, three coordination water molecules and five lattice water molecules. The Zn(II) exhibits three kinds of coordination modes, among which Zn(1) and Zn(3) ions have the same coordination number. Zn(1) is connected with nitrogen atom N(2) and oxygen atom O(4) of one Hmimda²⁻ ligand, and nitrogen atom N(5#3) and oxygen atom O(10#3) of another Hmimda²⁻ ligand, as well as one oxygen atom O(4W) from the coordination water molecule. However, Zn(3) is coordinated by two nitrogen atoms N(4), N(7) and two oxygen atoms O(8), O(14) of two different H₃mimda ligands, and one nitrogen atom (N8) from one bipy. Zn(2) is six-coordinated with nitrogen atoms (N1), N(3), N(6) and oxygen atoms O(2), O(6), O(12) from three different H₃mimda ligands. There are two crystallographically unique Tm(III) centers in the asymmetric unit, which show different coordination environments. Tm(1) is seven-coordinated by six carboxylate oxygen atoms O(1), O(1#1), O(3), O(3#1), O(5), O(5#1) from three H₃mimda, and one oxygen atom O(1W) from one coordinated water molecule in a pentagonal bipyramidal coordination geometry of TmO₇. The Tm(1)–O_{carboxyl} bond lengths vary from 2.212(7) to 2.256(7) Å and the Tm(1)–O_{water} bond length is 2.361(10) Å. Tm(2) is eight-coordinated by five oxygen atoms O(7), O(9), O(11), O(13), O(13#1), O(14) from three H₃mimda ligands and two other oxygen atoms O(2W), O3(W) from two coordinated water molecules, forming an

octahedral coordination geometry. The bond distances of Tm(2)–O range from 2.193(6) to 2.486(5) Å. The bond angles around each Tm(III) vary from 64.2(2) ° to 159.4(2) °. In addition, detailed hydrogen bonds of **1** are shown in Table 1, which all fall in the normal range of such weak interactions^[22].

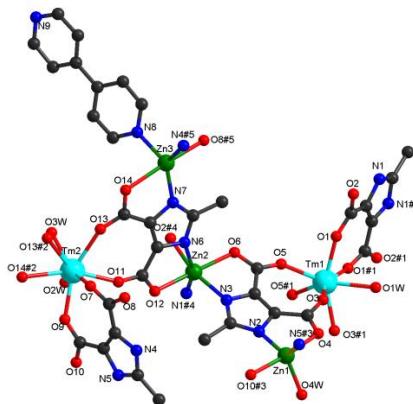
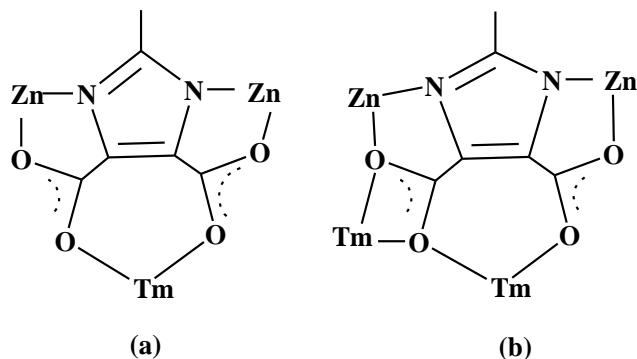


Fig. 1. Coordination environments of Tm and Zn atoms in the asymmetric unit of **1**.

All H atoms and the noncoordinated water molecules are omitted for clarity



Scheme 1. Coordination modes of free H₃mimda ligand in complex **1**

As indicated in Scheme 1, the mimda³⁻ anions adopt both μ_3 -kN, O: kO, O': kN', O' and μ_4 -kN, O: kN', O'kO, O': kO'', O'' coordination modes connected with the adjacent Tm(III) and Zn (II) ions. Each TmO₈ connects two neighboring Zn(II) chelate units through two H₃mimda ligands in two different modes to generate a 1D zigzag chain and further gives rise to a unique 2D Tm-Zn heteronuclear metal-organic network structure (Fig. 2b). In addition, six H₃mimda ligands link the neighboring Zn(II) ions *via* N,O-chelating composed of a [Zn₆(mimda)₆] ring with the bipy just acting as a terminal ligand leaving a free N atom. The [Zn₆(mimda)₆] rings are connected by one H₃mimda ligand to afford a 1D six-membered ring chain along the *b*-axis, as shown in Fig. 2c. The resultant 3D framework of **1** can be depicted as the Tm-Zn heteronuclear cages of [Tm₁₀Zn₁₀(mimda)₁₂(bipy)₂]_n linked with (TmO₇)_n through H₃mimda ligands of modes *a* and *b* (Fig. 3), and it is similar to other Ln compounds just reported^[23]. In the Tm-Zn heteronuclear cage, [Zn₆(mimda)₆] and [Tm₁₀(mimda)₆]_n are connected by H₃mimda ligand, leading to a "interlock" structure unit. After the hypothetical removal of guest water molecules, the total potential solvent-accessible void is found for this 3D framework of **1** to be 2025.8 Å³ per cell volume (accounting for 22.2% of the total unit cell system), calculated using the PLATON program^[24].

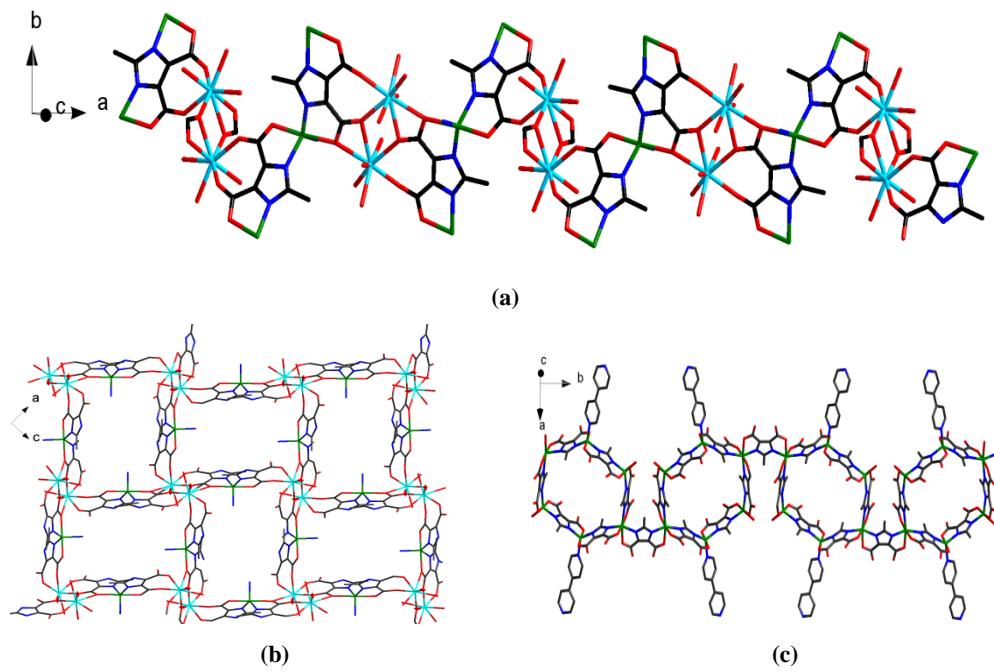


Fig. 2. (a) Schematic illustration of the 1D chain structure of 1 viewed along the bc plane; (b) Schematic illustration of the 2D interspersed structure of 1 viewed along the ac plane; (c) The bipy acts as a terminal ligand, leaving a free N atom, bridged at the $[Zn_6(mimda)_6]$ ring ends along the ab plane

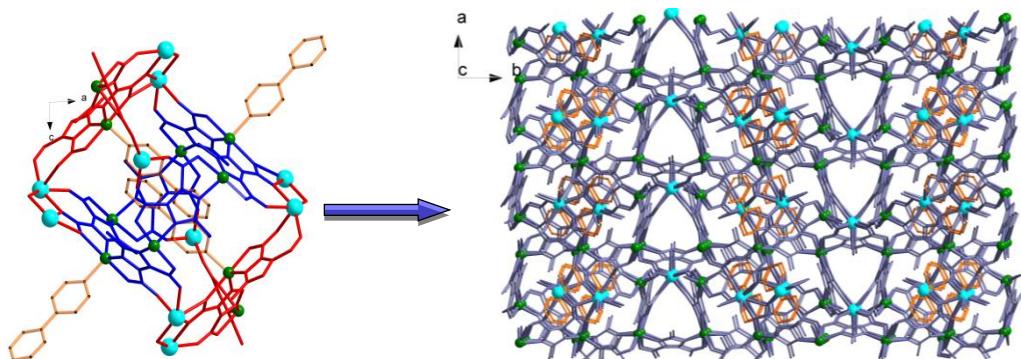


Fig. 3. 3D framework composed of Tm-Zn heteronuclear units 1 along the ab plane

3.2 Powder X-ray diffraction patterns and thermal stability

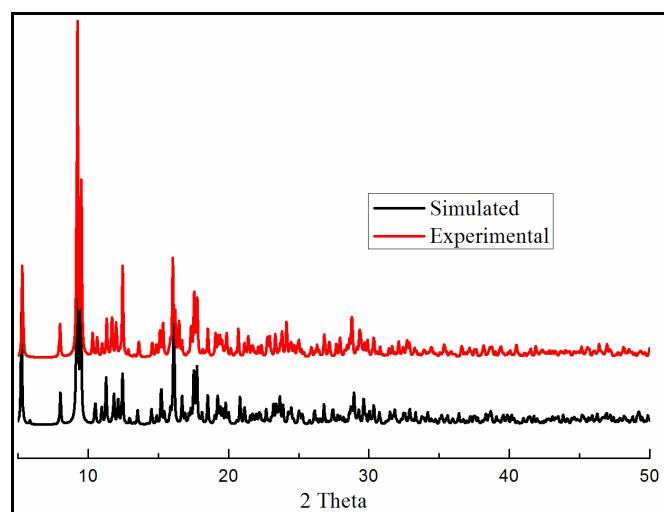
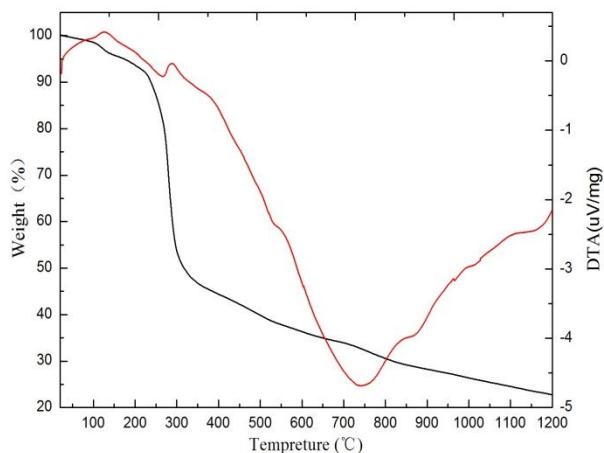


Fig. 4. Simulated and experimental PXRD patterns of complex 1

As shown in Fig. 4, powder X-ray diffraction pattern (PXRD) of complex **1** exhibits characteristic peaks at 2θ positions of 9.8, 12.2, 16.4, 18.3, 28.2 $^{\circ}$. The experimental pattern of complex **1** is basically consistent with the simulated one, indicating the phase purity of the synthesized bulk samples. Thermal gravimetric analysis (TGA) experiment was performed on a sample consisting of numerous single crystals from 30 to 1200 $^{\circ}$ C under N_2 atmosphere at a heating rate of 10 $^{\circ}$ C·min $^{-1}$. The TG and DTA curves are depicted in Fig. 5. Complex **1** firstly undergoes weight loss of 5.1% at about 175 $^{\circ}$ C due to the release of eight water molecules (calcd. 5.4%), and the framework decomposes at about 260 $^{\circ}$ C attributed to the departure of bipy moieties 11.7% (calcd. 10.6 %). Complex **1** continues to break down upon further heating and exhibits an obvious weight loss of H_3mimda ligands above 700 $^{\circ}$ C.

**Fig. 5. Thermal gravimetric analysis plot of complex 1**

3.3 Luminescence property

The luminescence properties of complex **1**, bipy and free H_3mimda ligand were investigated in the solid state at room temperature. As illustrated in Fig. 6, complex **1** exhibits an emission band with the maximum at 476 nm upon excitation at 325 nm. However, the maximum emission wavelength of H_3mimda ligand and bipy are 416 ($\lambda_{ex} = 315$ nm) and 363 nm ($\lambda_{ex} = 270$ nm), respectively. Compared with the free bipy and H_3mimda ligands, luminescence is probably originated from the ligand emission. The enhancement and significant red shift of the emission occur in complex **1**, which is probably due to the reaction between free ligands and metal ions, and further form the skeleton structure^[25-28].

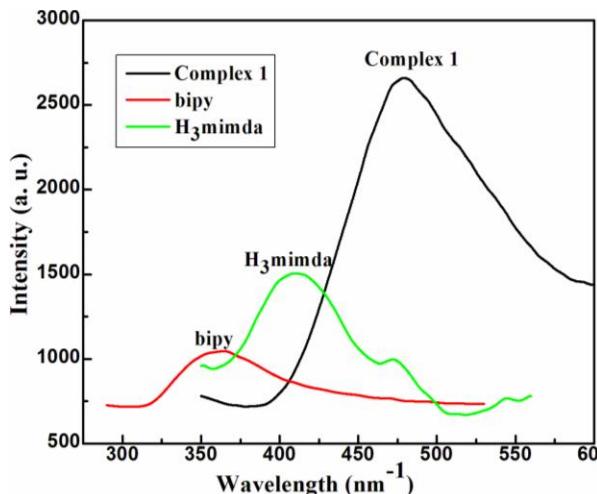


Fig. 6. Luminescent spectra of complex 1, bipy and H₃mimda ligand

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Structure and Luminescence Property

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A *d-f* heteronuclear metal-organic framework (MOF), $\{[\text{Tm}_3\text{Zn}_6(\text{bipy})_2(\text{mimda})_7(\text{H}_2\text{O})_3]\}(\text{H}_2\text{O})_5$ (1), H_3mimda = 2-methyl-1-H-imidazole-4,5-dicarboxylic acid, and bipy = 4,4'-bipyridine, has been synthesized under solvothermal conditions, and structurally characterized by elemental analysis, IR spectra and X-ray single-crystal diffraction.

